



Complete dechlorination of pentachlorophenol by a heterogeneous SiO₂–Fe–porphyrin catalyst

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ARTICLE INFO

Article history:

Received 25 November 2009

Received in revised form 27 December 2009

Accepted 7 January 2010

Available online 14 January 2010

Keywords:

Catalysis

Chlorinated compounds

Iron–porphyrin

Ferryl

Dechlorination

LC–MS

Heterogeneous

PCP

ABSTRACT

A highly efficient catalyst has been produced by immobilizing a biomimetic iron–porphyrin complex onto SiO₂. The catalyst was found to be highly efficient on the degradation of pentachlorophenol (PCP) achieving 100% of PCP decomposition within 2.5 h. Furthermore, complete dechlorination of the initial added PCP substrate was accomplished at the end of the reaction time. Dechlorination proceeded even after PCP was fully decomposed. The initial and main final metabolites of PCP decomposition were identified and a general catalytic mechanism is proposed.

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1. Introduction

Chloroaromatics, especially pentachlorophenol (PCP), are well known organochlorine compounds used extensively as insecticide, biocide, herbicide, pesticide and wood preservative. Chlorophenols, including PCP, have been listed as priority pollutants by the US Environmental Protection Agency [1] and European regulatory authorities [2]. They are well established as persistent toxic compounds for which the environment has little assimilative capacity. They are poorly biodegradable with a half-life up to some years in natural environment [3]. The resistance to degradation as well as the toxicity of chlorinated organic compounds increases with the number of halogen substituents [4]. Phenols with electron-withdrawing substituents, such as Cl, resist to oxidation i.e. they are usually characterized by high oxidation potential and low oxidation rate. Although their production and use were banned in several countries [5], chlorophenols were still found in many parts of the world [5,6]. They persist in wastewaters, in soils as well as in surface- and ground-waters, in many cases, far removed from the presumed point of entry [7,8]. This persistence is due to their resistance to biodegradation. Thus, efficient chemical

treatment processes are needed for the removal or transformation of such compounds to less harmful or biodegradable analogues.

Several remediation methods have been studied over the last years. Among them, chemical degradation methods are considered as the most promising and particularly the use of Fe-based biomimetic catalysts [9–11]. For the degradation of chlorophenols, metaloporphyrin derivative catalysts have mainly been used [9–11]. Iron–porphyrin catalysts are preferred because are generally more active [12,13]. Among the key-features for designing an efficient catalyst is its protection against oxidative deactivation due to the rapid self-oxidation under the highly oxidative conditions of the reaction [14–16]. Two main directions have been used to increase the stability towards oxidative self-destruction and to prevent catalyst deactivation caused by dimerization: (a) addition of substituents with electron-withdrawing and steric hindrance properties on the periphery of the porphyrin ring and (b) immobilization of the catalyst onto a suitable support.

In the field of heterogeneous catalysis, solid-supported metaloporphyrins have attracted much research attention since they (i) have increased stability and selectivity and (ii) they also can be easily recovered from reaction media and reused, minimising effluent contamination [17]. Furthermore, inorganic supports are more inflexible and hence should be more effective in preventing the catalyst deactivation caused by dimerization (μ-oxo dimers) [18]. Among the supports used to immobilize

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metalloporphyrins, inorganic supports such as SiO_2 are preferred for their low cost, availability, mechanical robustness and chemical inertness. Immobilization of the catalyst through covalent bonds is generally preferred vs. immobilization through electrostatic interaction of charged catalysts with charged support. Simply adsorbed catalysts suffer from leaching of the complex to solution and ensuing degradation [19]. Immobilization also prevents agglomeration of the catalyst. This ensures that only monomeric complexes are active for the degradation of the substrate. In addition immobilization can potentially lead to substrate shape-selectivity because of specific interactions of the substrates with the inorganic matrix [17]. More generally it has been shown that this technique can provide additional benefits arising from the steric and electronic effects of the support, which are in some respects analogous to the influence of the polypeptide chain in hemeproteins [20]. Our group, as well as others have already made a great deal of efforts on the heterogeneous catalysis and the results show that they are more efficient catalysts than the non-supported metalloporphyrins [21–26].

In this work, the use of an iron–porphyrin immobilized catalyst, $\text{SiO}_2\text{-FeR}_4\text{P}$ where R_4 corresponds to 2,6-di-*tert*-butylphenols at each meso-aryl position of the porphyrin ring, for the decomposition of PCP is presented. In our previous work [24] the properties of the active center for the homogeneous FeR_4P and heterogenised $\text{SiO}_2\text{-FeR}_4\text{P}$ catalyst were studied. In the present work we focus on the mechanism of PCP degradation and the oxidation products. In this context, analytical chromatographic data including detailed Cl release measurements revealed that complete dechlorination of the initial added PCP is achieved by the heterogeneous $\text{SiO}_2\text{-FeR}_4\text{P}$ catalyst. In addition, the initial and major final metabolites of PCP decomposition were identified. The mechanism of the catalytic PCP degradation is discussed. Thus the aims of the present work were: (a) to study the mechanism of dechlorination of PCP by the $\text{SiO}_2\text{-FeR}_4\text{P}$ catalyst, (b) to identify the initial and major final metabolites, (c) to explore the mechanism of PCP degradation by the $\text{SiO}_2\text{-FeR}_4\text{P}$ catalyst.

2. Experimental

All solvents and reagents were of commercial grade unless otherwise stated and were purchased from Merck and Aldrich.

2.1. Synthesis

The catalyst FeR_4P , was synthesized by known procedures as described previously [27,28] and purified by silica gel column chromatography using CHCl_3 , 80% CHCl_3 and 20% hexane as the eluting solvents. Immobilization of the metalloporphyrin FeR_4P was performed on a modified by imidazole 3-(glycidyloxypropyl) silica-supported on SiO_2 . The metalloporphyrin ligation to the functionalized SiO_2 was achieved by stirring a CH_2Cl_2 solution of a known amount of metalloporphyrin into a suspension of the support for 24 h. The resulting supported catalyst ($\text{FeR}_4\text{P-SiO}_2$) was washed with CH_2Cl_2 to remove unbound catalyst and weakly bound porphyrin and dried for 3 h at 60 °C. The loadings were quantified by measuring the amount of unloaded metalloporphyrin in the combined reaction solvent and washings by UV–vis spectroscopy. Detailed description of the procedure used can be found elsewhere [27,28].

2.2. HPLC/LC–MS analysis

Quantitative HPLC determinations for PCP were performed with a Dionex P680 HPLC chromatograph equipped with a Dionex 1024 Diode Array Detector. The column used was Acclaim C18 5 μM , 120 Å, 4.6 mm \times 250 mm and was thermostated at 23 °C. The HPLC

mobile phase was a mixture of an aqueous (Milli-Q) solution of 0.8% H_3PO_4 and acetonitrile (15/85, v/v) with a flow rate of 1 ml/min. PCP was measured at 210 nm. The following wavelength channels were also monitored through out the reaction time for the detection of any oxidation products: 255 nm, 287 nm, 295 nm and 315 nm. LC–MS analysis of the final products were performed on an Agilent 1100 instrument equipped with a C8 Zorbax column (4.5 mm \times 150 mm) with a mobile phase $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (90/10, v:v).

2.3. Ion chromatography (IC) analysis

Determination of Cl^- ions released during the oxidation of PCP was performed with a Dionex ICS-1500 ion chromatography system equipped with ASRS Ultra II self-regenerating suppressor. The column used was IonPac AS9-HC and the mobile phase was 9 mM aqueous sodium carbonate.

2.4. General catalytic procedures

All reactions were performed in test tubes of 4 ml equipped with a magnetic stirrer at room temperature. A typical reaction mixture contained 187.5 μM PCP (100 μl of a 3.75 mM acetonitrile stock solution), 18.7 μM of the catalyst (0.0032 g of the immobilized i.e. catalyst:substrate ratio = 10%), 2.34 mM of the oxidant (23.4 μl of a 200 mM NaIO_4 aqueous stock solution i.e. 12.5 equivalents of oxidant with respect to the substrate), 187 μM or 37.5 μM of imidazole as co-catalyst (37.4 μl and 7.5 μl respectively of 10 mM aqueous stock solution i.e. 10 or 2 equivalents respectively of imidazole with respect to the catalyst). Imidazole is often used as co-catalyst in Fe–porphyrin catalysts playing a dual role i.e. as axial ligand to the iron, or as acid–base catalyst [18]. For all reactions tested, the appropriate volumes of acetonitrile and milli-Q water were added so that the final volume of the reaction was 2 ml and the ratio acetonitrile: H_2O equal to [3:1] [v:v], unless otherwise mentioned. Acetonitrile was used as co-solvent to solubilize the hydrophobic PCP. In all cases the oxidant was the last reagent added. For the experiments to monitor Cl^- ions release, the volume of the reaction was five times larger (i.e. 10 ml) keeping the other reaction conditions constant. The quantification of PCP by HPLC and of Cl^- by IC was based on comparison with standards. For the quantification of PCP and Cl^- small aliquots were extracted after centrifugation of the reaction mixture. The stability of the catalyst was studied in detail, as reported in reference [29]. Under the conditions of the experiments described herein, dissolution of the catalyst was <5%.

3. Results

3.1. PCP conversion and Cl^- release

The $\text{FeR}_4\text{P-SiO}_2$ catalyst was found to be a very efficient catalyst for PCP decomposition [24]. As shown in Fig. 1A, 100% conversion of PCP was accomplished within 2.5 h by the [$\text{FeR}_4\text{P-SiO}_2/\text{NaIO}_4$] system, corresponding to a turnover frequency (TOF) of 5 turnovers/h. No conversion of PCP was observed in the control experiments, i.e. in the presence of either NaIO_4 or the catalyst alone. In the same experiments, the release of Cl^- ions – during catalytic oxidation of PCP – was monitored by means of IC. As shown in Fig. 1A, PCP disappearance is followed by production of Cl^- ions by the [$\text{FeR}_4\text{P-SiO}_2/\text{NaIO}_4$] system. However, no production of Cl^- ions was observed in the control experiments. These results indicate that the disappearance of PCP can be attributed to catalytic oxidative dechlorination by the $\text{FeR}_4\text{P-SiO}_2$ catalyst. Fig. 1B shows the molar ratio of [Cl^-] released vs. the amount of [PCP] disappeared ($[\text{Cl}^-]/\Delta[\text{PCP}]$), where $\Delta[\text{PCP}] = [\text{initial PCP concentration } [\text{PCP}]_0] - [\text{PCP remained at time } t ([\text{PCP}]_t)]$.

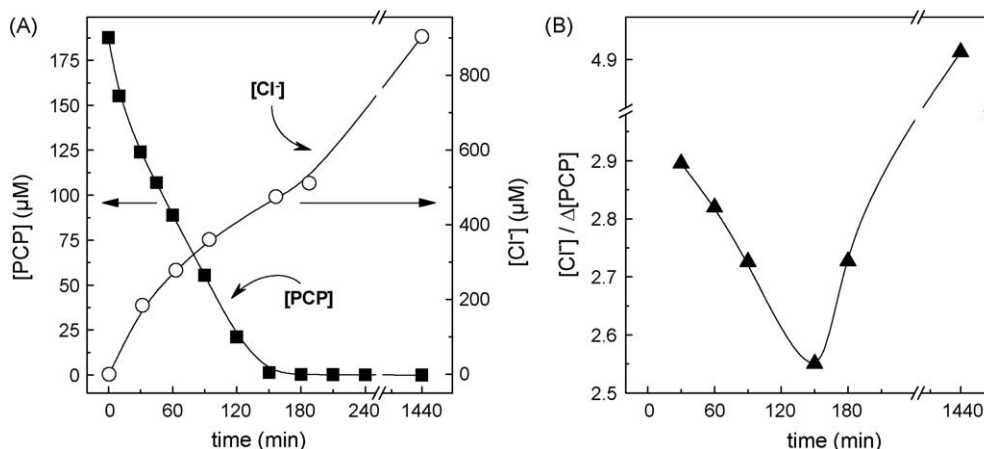


Fig. 1. (A) Catalytic decomposition of PCP (■) and release of Cl⁻ (○) by the Fe₄P-SiO₂/Imidazole/NaIO₄ system. (B) Time-dependence of the [Cl⁻]/Δ[PCP] ratio. Catalytic conditions: [Cat/PCP/Imid/NaIO₄] = [1/10/10/125].

At $t = 2.5$ h i.e. where the PCP concentration dropped to zero (Fig. 1A), the molar ratio $[Cl^-]/\Delta[PCP]$ was 2.53 (Fig. 1B). Despite the fact that at that time (reaction time = 2.5 h) the conversion of PCP by the heterogenised Fe₄P catalyst was 100%, the dechlorination process appeared to further evolve: within 24 h the molar ratio $[Cl^-]/\Delta[PCP]$ was 4.91, see Fig. 1B. The $[Cl^-]/\Delta[PCP] = 4.91$, $t = 24$ h, corresponds to 98% dechlorination of the initial PCP added to the reaction mixture. These data indicate that chlorinated intermediate compounds are produced after PCP degradation. Then, after complete conversion of PCP, the release of Cl⁻ ions indicates that the formation of the initial by-products does not affect their dechlorination.

Fig. 1B shows the time-rate of the number of Cl⁻ atoms released per PCP molecule converted. Two regimes appear: (a) from $t = 0$ to 2 h, the molar ratio $[Cl^-]/\Delta[PCP]$ decreases monotonically (i.e. from 2.9 to 2.53) until the point where PCP is fully converted, $t = 150$ min = 2.5 h in Fig. 1A. (b) From that point and on, this trend was inverted and an increase of the ratio $[Cl^-]/\Delta[PCP]$ was observed (i.e. from 2.53 to 2.73 and 4.91 at $t = 2.5$ h, 3 h and 24 h respectively). For a proper analysis of this intriguing non-linear behavior, the reaction products had to be identified. This will be discussed in detail in Section 3.2.

The initial axial ligand of the homogeneous Fe₄P catalyst – that is before the immobilization – is a Cl atom [24]. However, as we have shown in our previous work, during the immobilization of the homogeneous catalyst via axial coordination to IGOPS (see Section 2.1) the Cl atom is displaced [29]. Hence, the heterogeneous catalyst is chlorine-free and the observed Cl⁻ release during the catalytic reaction derives exclusively from the oxidative dechlorination of PCP.

At this point is of pertinence to compare the dechlorination efficiency of the SiO₂-Fe₄P catalyst with the literature data. So far, the best iron-porphyrin catalyst reported in the literature for oxidative decomposition of chlorophenols performed much lower dechlorination (1.43 Cl⁻ released per PCP molecule converted) [12]. In other studies, the number of chlorine atoms abstracted from PCP by similar catalytic systems [30] and with the use of additives [31] has also been reported to be significantly smaller (1.3–1.8 and 2.75–3.12 respectively) than in the present work.

3.2. Oxidation products

3.2.1. Initial products

Under the conditions of our experiments, PCP exhibits electronic absorption maxima at 210 nm. Incubation of PCP with the Fe₄P-SiO₂/NaIO₄ system resulted in significant time-depen-

dent spectral changes of the HPLC chromatogram, characterized by loss of PCP absorption maxima and increased absorbance at different wavelengths. In contrast, no absorbance changes were observed when PCP was incubated with NaIO₄ or Fe₄P-SiO₂ alone. The observed new features correspond to the product profile of the catalytic reaction. No traces of less-chlorinated phenols in the catalytic solution could be detected by HPLC e.g. based on comparison of chromatograms of the reaction mixture with commercial standards. A single major product was detected at initial catalytic times, $t < 30$ min, which was virtually absent in reaction mixtures without the catalysts or the oxidant. This major product showed a λ_{max} at 287 nm, assigned to tetrachloro-1,4-benzoquinone (TCQ), based on the identical UV absorption spectra (Fig. 2) obtained using a Diode Array Detector of our HPLC. The formation of TCQ directly demonstrates that a decrease of the toxicity is accomplished [32] as anti-fungal activity of PCP has been found to be at least five times greater than that of the TCQ.

As it was demonstrated in Fig. 1, oxidative dechlorination of PCP takes place during the catalytic degradation, which is essential for the

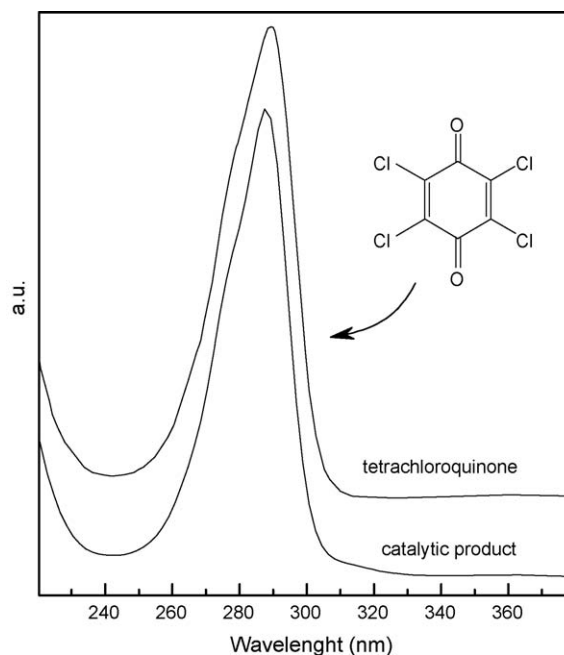


Fig. 2. Electronic absorption spectrum of tetrachloro-1,4-benzoquinone and of major metabolite of PCP decomposition.

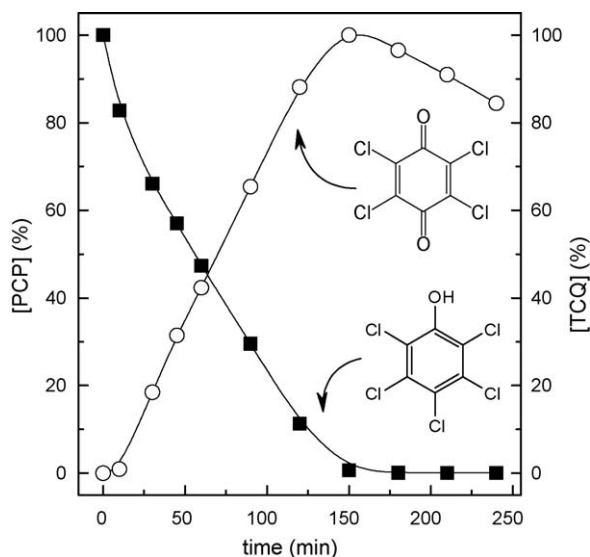


Fig. 3. Time-dependence of [PCP] loss (■) and [TCQ] generation (○).

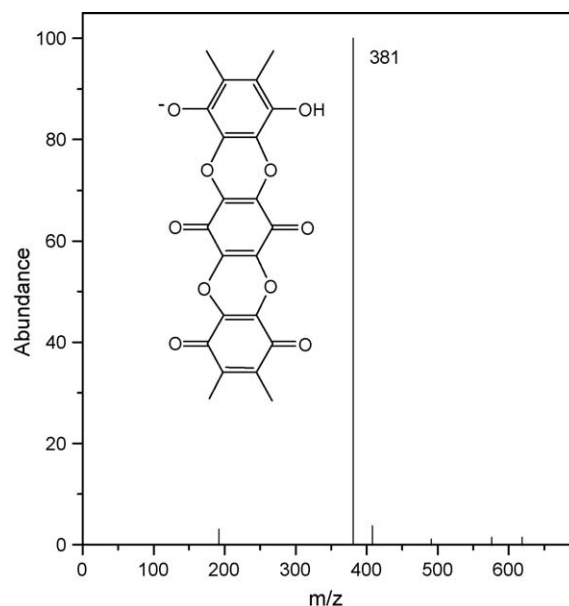


Fig. 4. Mass spectrum of the catalytic reaction mixture after 24 h incubation.

formation of TCQ. Production of TCQ has been previously observed during the oxidative decomposition of PCP by horseradish peroxidase and H_2O_2 [33] and has been suggested as an intermediate in PCP degradation by similar synthetic iron–porphyrin catalysts [12]. Formation of a quinone has also been observed for less-chlorinated phenols such as 2,4,6-trichlorophenol (TCP) forming 2,6-dichloroquinone in catalytic systems using similar synthetic Fe–porphyrin catalysts [11–13,34,35] or lignin peroxidase [36]. Furthermore, the formation of TCQ explains the inability to detect less-chlorinated phenols in the reaction mixture. In summary, based on the above information, it is concluded that one of the initial product of PCP decomposition by the $\text{FeR}_4\text{P-SiO}_2/\text{NaIO}_4$ system is TCQ.

The time-dependent analysis of HPLC chromatogram, Fig. 3, shows that the disappearance of PCP—detected at 210 nm—matches the corresponding time-dependent increase of the product – TCQ – observed at 287 nm. The kinetics of their relative intensities during the catalytic reaction is presented in Fig. 3. A gradual increase of TCQ can be seen following PCP decomposition. The maximum intensity of TCQ was observed when the concentration of PCP was zero (t 2.5 h). From that point and on, a decrease of [TCQ] was observed. This is in agreement with the data presented in Fig. 1A where the release of Cl^- proceeds after the total conversion of PCP. Finally, it is worth mentioning that at the end of the reaction time (t 24 h) the signal of TCQ was not detectable. However, at reaction

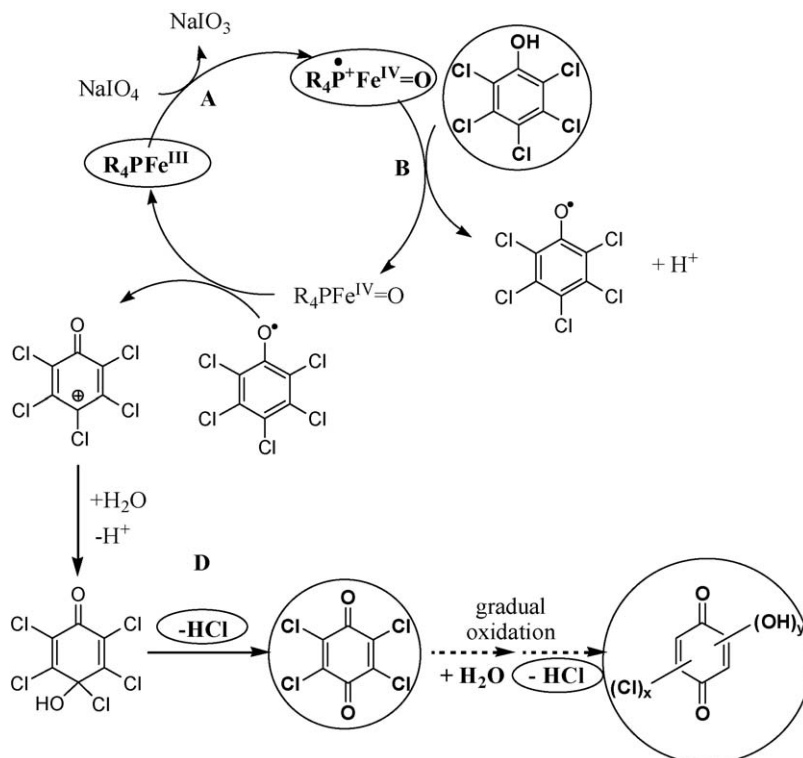


Fig. 5. Proposed catalytic cycle for PCP degradation by the $\text{FeR}_4\text{P-SiO}_2/\text{NaIO}_4$ system. Encircled are shown the moieties directly detected.

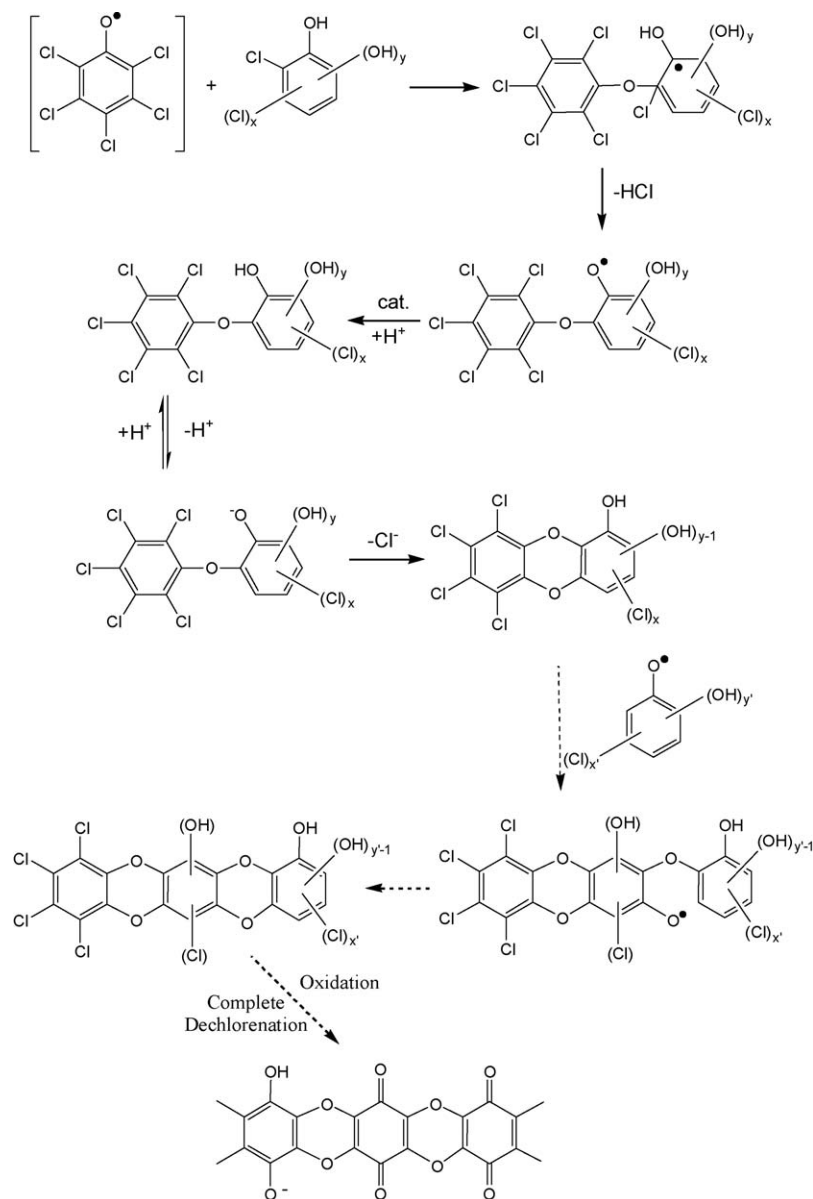


Fig. 6. Proposed reaction mechanism for the production of the trimmer $C_{18}O_{10}H_5$.

time 2.5 h, where PCP is fully converted, the chlorine atoms released per PCP molecule is 2.53. This indicates that besides TCQ other products are also formed during that time, since for the production of one TCQ only one Cl^- atom must be released per PCP molecule converted. Moreover, the kinetics presented in Fig. 3 clearly indicate that when PCP is present in the reaction mixture, the kinetics of TCQ oxidation is much slower than the kinetics of its formation. In other words, TCQ accumulates during oxidation of PCP. This is in agreement with the literature reports for less-chlorinated phenols where the oxidation of the quinone formed, takes place after complete oxidation of the chlorophenols [11].

A close inspection of Fig. 3 reveals that at initial reaction times (i.e. t 10 min), the increase of [TCQ] does not follow the decay of [PCP]. For example, at t 10 min, the loss of PCP was $\sim 20\%$ while the formation of TCQ was less than 3%. Furthermore, the decay of [PCP] has $t_{1/2} \sim 55$ min, while the $t_{1/2}$ of [TCQ] formation is $t_{1/2} \sim 70$ min. This indicates that the formation of TCQ requires more than one step following the conversion of PCP and will be further analyzed in Section 4.

3.2.2. Final products

The chemical nature of the final products was determined by LC–MS spectroscopy. Mass spectra of the reaction mixture were analyzed at the end of the catalytic reaction (t 24 h). The MS data ruled out the formation of clorodibenzodioxins and chlorodibenzofuran. LC–MS spectroscopy revealed one major product with a very intense anion at m/z 381 (Fig. 4). The pattern of the MS spectra revealed the absence of Cl at the final product, in agreement with the experiments of Cl^- release (Fig. 1). The product was tentatively assigned to a Cl-free anionic trimmer ($C_{18}O_{10}H_5$). Polymerization phenomena forming dimeric and trimeric products have been reported during oxidative decomposition of PCP and less-chlorinated phenols [9,12].

4. Discussion

Under the conditions of our experiment, the $Fe_4P-SiO_2/NaIO_4$ system was found to be very efficient for the decomposition of PCP. Complete conversion of the substrate was accomplished within 2.5 h. Experiments measuring the release of Cl^- have shown that

dechlorination proceeds after the fully transformation of PCP (Fig. 1A) and complete dechlorination of the initial substrate is accomplished within 24 h of the reaction. The initial product of PCP decomposition was identified as a tetrachloro-1,4-benzoquinone produced after the first dechlorination of PCP. The main final product was tentatively assigned to a trimmer ($C_{18}O_{10}H_5$).

4.1. Mechanistic aspects

Based on the data presented above it is concluded that the initial product of PCP decomposition by the FeR_4P-SiO_2/NaO_4 system is TCQ. In our previous work [24] we have shown that the active intermediate specie of the FeR_4P-SiO_2 catalyst responsible for the decomposition of PCP is an oxo- Fe^{IV} -porphyrin π -cation radical specie ($[Fe^{IV} = O \text{ Por}^{\bullet}]$), similar to Compound I of heme enzymes. Moreover, dechlorination of PCP takes place during the catalytic reaction (Fig. 1). Based on this information, a hypothetical reaction mechanism of the initial steps of the catalytic decomposition of PCP involving all the above-mentioned steps is presented in Fig. 5. To facilitate the discussion, the moieties directly detected are encircled.

The mechanism in Fig. 5 involves (a) an initial dechlorination of PCP and production of TCQ. Both these phenomena have been experimentally observed (Figs. 1A and 2). (b) Then the reaction mechanism involves two one-electron steps. Reduction of the oxo- Fe^{IV} (ferryl)-porphyrin π -cation radical ($[Fe^{IV} = OR_4P^{\bullet}]$), that is the active intermediate specie of the catalyst [24], occurred in the presence of a substrate molecule (step B) after the oxidation of the initial state of the catalysts $Fe^{III}R_4P$ by NaO_4 (step A). This active intermediate has been detected by EPR spectroscopy [24]. (c) This produces a radical on a substrate molecule and $[Fe^{IV}R_4P]$ by a one-electron transfer step. (d) Further one-electron oxidation of the pentachlorophenoxy radical by $[Fe^{IV}R_4P]$ leads to the initial state of the catalyst ($Fe^{III}R_4P$) and the generation of a cation substrate intermediate (step C).

The oxidative dehalogenation of chlorinated phenols by chloroperoxidase has been shown to involve two consecutive one-electron steps from the two forms $[Fe^{IV} = O \text{ Por}^{\bullet}]$ and $[Fe^{IV} = O \text{ Por}]$ rather than a single two-electron oxidation [37]. Nucleophilic attack of a water molecule at the 4-position of the substrate's cation intermediate followed by deprotonation and elimination of HCl results in the formation of TCQ (step D) (Fig. 5). Subsequent steps can lead to further dechlorination. The oxidation of PCP via a phenoxyl radical to the corresponding para-quinone has been reported for many enzymes [38].

In Fig. 5 it can be seen that after the initial transformation of PCP, three steps are required for the formation of TCQ. These are: the formation of (a) a phenoxyl radical, (b) a cation intermediate and (c) attack by a water molecule. These three steps can explain the delay of TCQ formation compared with the loss of PCP observed in Fig. 3.

On the basis of the LC-MS data and the structure of the main final product, the pathway of PCP decomposition by the FeR_4P-SiO_2/NaO_4 system is proposed to be as shown in Fig. 6. The formation of TCQ has been suggested as a possible precursor for polymer formation [39]. The trimmer is formed through subsequent steps of dechlorination and oxidative couplings via the formation of radicals (Fig. 6). Formation of dimers including polychlorinated phenoxyphenols and chlorinated polyhydroxybiphenyls as well as dimeric and trimmeric products derived from intermediate phenoxy radicals, has been previously reported during the oxidative transformation of polychlorinated phenols using similar biomimetic [9,12] or different catalytic systems [40–42]. In an analogous manner, formation of the proposed trimmer

can take place under the oxidative conditions of our experiment where radicals are being formed.

5. Conclusions

This study reports the first example of complete dechlorination of PCP. The initial and the major final products of PCP decomposition were identified as a tetrachloro-1,4-benzoquinone and a non-chlorinated trimmer respectively. Catalytic mechanisms for the production of the initial as well as the final product were also proposed.

Acknowledgements

We thank Dr. A. Badeka for mass spectra obtained on a machine funded by the Network of Horizontal Laboratory and Unit Centres of the University of Ioannina.

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